

# PATENT SPECIFICATION

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## COMPLETE SPECIFICATION

### NO DRAWINGS

### Process for the Production of Catalytically Active Coatings on Reaction Chambers

We, LONZA ELECTRIC AND CHEMICAL WORKS LTD., of Gampel, Kanton Wallis, Switzerland, a body corporate organised under the laws of Switzerland, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

10 This invention relates to the production of catalytically active coatings on reaction chambers.

For the synthesis of hydrocyanic acid from ammonia and methane at temperatures from, for example, 900 to 1400°C., it is known to use elongated reaction chambers, more especially tubes, in which those walls that are swept over by the gases are lined with catalysts. As catalysts there are usually employed metals of the platinum group, i.e. ruthenium, rhodium, palladium, osmium, iridium or platinum, which can advantageously be alloyed with other metals or be mixed with oxides, such as  $Al_2O_3$ . The coatings which adhere to the walls are formed by introducing solutions of metal compounds, for example of Al, Cu, Pt or of the other metals of the platinum group alone or in admixture into reaction vessels, for example into horizontally-arranged tubes, whereupon the reaction vessels, for example tubes, are heated while being rotated and while discharging the evaporated solvent through axial openings or gas outlet pipes extending through the tube closures. In this way, dried metal salt coatings are obtained as an intermediate stage. In order to produce the required thickness of 10 to 30, preferably 20 mg. of platinum metal per square centimetre of active surface, this operation is repeated several times. The coatings thus produced are then heated above the decomposition temperature of

the metal salt to provide the catalyst. The heating may be carried out with or without 45 passage of non-oxidising gases or air through the vessel, or in a current of gases such as  $H_2$ ,  $NH_3$ , or  $N_2$ .

It has been found that the known coatings of aluminium oxide and metals of the platinum group must be produced and activated in a specific manner in order to obtain very active and durable catalysts.

The present invention provides a process for the production of catalytically active coatings on the walls of reaction chambers for the synthesis of hydrocyanic acid from ammonia and methane at temperatures from 900 to 1400°C. comprising treating the walls with a hydrochloric acid solution containing aluminium and a metal of the platinum group, evaporating the solvent and drying the deposited material, repeating the treating, evaporating and drying until sufficient layers of the metal of the platinum group and  $Al_2O_3$  have been deposited, heating the coating obtained up to 800°C. in a current of a reducing gas and activating the resulting catalyst by heating at 900 to 1400°C. for several days in such a way that first only ammonia is passed over the catalyst and that methane is added at such a rate that the methane content in the gases, after passage over the catalyst and after removal of  $NH_3$  and  $HCN$ , never exceeds 1% by volume and that not earlier than after 4 days a volume ratio of  $NH_3$  to  $CH_4$  of 1 to 0.7-0.8 is reached.

Preferred reducing gases are ammonia and hydrogen.

In this way, hard durable coatings of porous  $Al_2O_3$  with metals of the platinum group homogeneously dispersed through them are obtained. Because the metals of the platinum group are embedded in the aluminium oxide layer, losses of these

metals during operation are largely avoided and thereby the activity of the catalyst is considerably extended. It is possible by this working method to shorten the activation period and to avoid differences of activity between different tubes. Furthermore, by this method of activation, the formation of carbon black and a consequent undesired carbonisation of the platinum coating is avoided. It has in fact been found that the formation of carbon black may lead to reduction of the  $\text{Al}_2\text{O}_3$  to metallic aluminium, which, in turn, may form alloys (for example  $\text{PtAl}_2$ ) or aluminium nitride. It has further been found that with an increased formation of carbon black, the resulting metal alloys are obtained in the form of small balls, which travel down into the lower parts of the reaction tube. In particular, it was found that with catalysts contaminated with carbon black, there was a disadvantageous decrease in the activity during operation because of the migration of the metals of the platinum group into the lower part of the tube and alteration of the wall of the tube.

The carbon black is formed by decomposition of the methane. The incorporation of carbon black into the catalytic coating must, however, be avoided during the activation of the catalyst. This is effected according to the invention by increasing the methane content so slowly that the content of methane in the residual gas freed from  $\text{NH}_3$  and HCN does not exceed 1% by volume and the ratio of  $\text{NH}_3$  to  $\text{CH}_4$  of 1 to 0.7-0.8 is only reached after at least four days. Nevertheless, should some carbon black be fortuitously formed by damming up of reaction gases in the tube, the activation must be stopped and the coating of carbon black formed in the upper part of the reaction tube must be removed by treatment with air at about  $900^\circ\text{C}$ . and then the activation must be continued in the manner indicated above.

The production of the anhydrous coatings by removing the solvent while heating is an operation known in the art. Depending upon the temperature and the heating period, the salts are partially decomposed to form  $\text{Al}_2\text{O}_3$  and metals of the platinum group.

#### Example 1

The inside wall of a tube made of sillimanite with a diameter of 40 mm. and a length of 1500 mm. is treated with a hydrochloric acid solution of Al, Pt and Ru, the aluminium content, calculated as  $\text{Al}_2\text{O}_3$ , being 4.25% by weight and the content of Pt and Ru, calculated as  $\text{Pt}_{10}\text{Ru}_{10}$ , being 4% by weight. The horizontally disposed tube is charged with the solution and then, with gentle heating, is slowly rotated about the tube axis or an axis parallel thereto. The

heating is effected uniformly, for example with hot gas, from a series of small flames, or electrically. The vaporisation of the solution is accelerated by some air being conducted through the tube. After evaporation of the solution and drying the residue while heating to  $150^\circ\text{C}$ ., a dry coating of  $\text{Al}_2\text{O}_3$  and the salts of platinum and ruthenium is left. The tube with the coating thus obtained is now heated up to  $800^\circ\text{C}$ . in an annealing furnace while passing a small quantity of ammonia therethrough; it is then left to cool. The said operation of impregnation, heating up to  $150^\circ\text{C}$ ., allowing to cool and annealing up to  $800^\circ\text{C}$ . is repeated five times.

In this way, a coating is obtained which consists of a porous aluminium oxide layer in which the platinum and ruthenium are finely dispersed and which is completely free from chlorine.

The coating is now activated by the tube with the catalyst layer being heated in a molybdenum furnace to an average temperature of  $1200^\circ\text{C}$ . Simultaneously, a stream of 400 litres of ammonia per hour is conducted through the tube; methane is then added, the supply of methane being increased so slowly that the methane content in the residual gas freed from  $\text{NH}_3$  and HCN never exceeds the value of 1% by volume. As the activation progresses, the addition of methane can be so increased within 8 days that the volume ratio between ammonia and methane reaches 1:0.7-0.8. The activation in the activating furnace is now completed and the reaction tube is ready for fitting into the reaction furnace. For carrying out the reaction, there are preferably used two concentric tubes fitting one within the other, the reaction gases being conducted through the annular space between the two tubes. In this case, the inner tube must also be coated on the outside wall with the catalyst layer and be activated.

#### Example 2

Two concentric sillimanite tubes are used; the outer reaction tube has a diameter of 40 mm. and a length of 2000 mm. is closed at one end and closed against the inner tube at the other end. It is provided with a radial discharge aperture. The inner sillimanite tube has an internal diameter of 28 mm. an external diameter of 33 mm. and a length of 2200 mm. and is open at both ends. The reaction gases are introduced from above through the inner sillimanite tube, they then enter the annular space at the bottom end, which is formed by the tubes arranged concentrically one within the other, and leave again at the radial discharge aperture.

The inner wall of the outer reaction tube, which is externally heated, and also the

inner and outer walls of the inner tube are coated with salts of aluminium and metals of the platinum group according to the invention and further treated as indicated below:

For coating purposes, there is employed a hydrochloric acid solution of Al, Pt and Ru; the aluminium content, calculated as  $\text{Al}_2\text{O}_3$ , is 1% by weight and the content of Pt and Ru, calculated as  $\text{Pt}_{83}\text{Ru}_{17}$ , is 4% by weight.

The two horizontally disposed tubes are wetted with the said solution for coating the inner wall and are then slowly rotated about the tube axis while heating gently. The heating is effected uniformly by means of electric resistance heating or by means of hot gases; the evaporation of the solution is accelerated by some air being conducted therethrough. After evaporation of the solvent and after drying the residue while heating to about  $150^\circ\text{C}$ ., a dry coating of the said salts is left.

For coating the outside wall of the inner tube, the solution is applied in somewhat more concentrated form by means of a brush to the external wall thereof. The tube is rotated at the same time and heated to  $100$  to  $120^\circ\text{C}$ ., so that the solution rapidly evaporates and solution can be applied again to the dried areas by means of the brush. After the necessary layer thickness has formed, a dry uniform coating of these salts remains on the tube after heating to about  $150^\circ\text{C}$ .

2 mg. per square centimetre of platinum and ruthenium calculated as  $\text{Pt}_{83}\text{Ru}_{17}$  are applied in one impregnation stage. With the use of this relatively small amount, a completely uniform and firmly adhering coating of  $\text{Al}_2\text{O}_3$  and  $\text{Pt}_{83}\text{Ru}_{17}$  is obtained.

In order to obtain the necessary quantity of catalyst layer on the walls of the tube, the impregnation is repeated several times.

A total of 20 mg. per square centimetre of platinum and ruthenium is applied to the externally heated active tube wall of the reaction tube by repeated coating in 10 stages.

Approximately 16 mg. of metals of the platinum group per square centimetre of active surface are sufficient for the outer wall of the inner tube, and about 8 mg. of metals of the platinum group for the same surface area for the inner wall.

The quantities of metals of the platinum group per square centimetre as indicated above are average values; quantities in excess of or less than the aforesaid quantities can be used. Instead of using a quantity of 20 mg., it is possible to employ a quantity between 10 and 30 mg. per square centimetre. The corresponding replacement values for 16 mg. and 8 mg. per square centimetre, respectively, are 8 to 20 mg.

per square centimetre and 6 to 12 mg. per square centimetre, respectively.

It has proved to be advisable always to use for the last impregnation step a hydrochloric acid solution containing only metals of the platinum group and no aluminium.

The coatings obtained in the manner described are now activated. The reaction tubes are heated in an electrically heated furnace to an average temperature of  $1200^\circ\text{C}$ . while passing through a current of 400 litres of ammonia per hour. Methane is then added to the ammonia, the supply of methane being increased so slowly that the methane content in the residual gas which issues from the outer reaction tube and is freed from  $\text{NH}_3$  and  $\text{HCN}$  never exceeds the value of 0.3% by volume.

Within an activation period of 8 days, the supply of methane can be so increased that the volume ratio between ammonia and methane reaches a value of 1:0.7. The activation is thereafter completed in the activating furnace and the reaction tube is ready for installation in the reaction furnace.

The tubes activated in the manner which has been described after being installed in the reaction furnace, are brought to full load in stages, it being possible for the volume ratio of  $\text{NH}_3:\text{CH}_4$  achieved in the activation to be further increased to 1:0.8.

The reaction spaces provided with catalyst composition produced according to Examples 1 and 2 have been installed in a furnace for carrying out the synthesis of hydrocyanic acid. A mixture of ammonia and methane was then conducted at a temperature of about  $1200^\circ\text{C}$ . through these spaces and the gas mixture containing hydrocyanic acid was removed on leaving the said spaces or chambers. After an operational period of 12 months, the activity of the catalyst had still remained completely unchanged and it was not possible to detect any formation of carbon black.

It has not been found to be advisable for separate solutions of the aluminium salt and of the salt of the metal platinum group to be applied sequentially to the walls of the reaction chambers, since this procedure does not provide a homogeneous layer in which the metals of the platinum group are finely dispersed in the aluminium oxide layer. Such a homogeneous layer is necessary if the catalyst is to be a good one. In theory, it would be possible to conceive of such solutions being applied alternately in very thin layers to the tubes, and of thereby being able to obtain an adequate degree of homogeneity. In practice, however, the coating would have to be carried out a very large number of times, for example 50 to 100 operations, in order to obtain an adequate layer thickness.

With the concentrated solutions used in practice, the impregnation should be repeated at least 5 and preferably 5 to 12 times in order to obtain the required thickness of layer.

5 With more dilute solutions, the number of repetitions is greater.

10 Instead of the sillimanite tubes referred to in the Example, it is also possible to employ tubes of other ceramic materials, for example clay tubes.

WHAT WE CLAIM IS:—

1. A process for the production of catalytically active coatings on the walls of  
15 reaction chambers for the synthesis of hydrocyanic acid from ammonia and methane at temperatures from 900 to 1400°C., comprising treating the walls with a hydrochloric acid solution containing  
20 aluminium and a metal of the platinum group, evaporating the solvent and drying the deposited material, repeating the treating, evaporating and drying until sufficient layers of the metal of the platinum group

and  $\text{Al}_2\text{O}_3$  have been deposited, heating the  
25 coating obtained up to 800°C. in a current of a reducing gas and activating the resulting catalyst by heating at 900 to 1400°C. for several days in such a way that first only ammonia is passed over the catalyst  
30 and that methane is added at such a rate that the methane content in the gases, after passage over the catalyst and after removal of  $\text{NH}_3$  and  $\text{HCN}$ , never exceeds 1% by volume and that not earlier than after 4  
35 days a volume ratio of  $\text{NH}_3$  to  $\text{CH}_4$  of 1 to 0.7-0.8 is reached.

2. A process as claimed in claim 1, substantially as described with reference to either of the Examples.

3. Reaction chambers when produced  
40 by a process as claimed in either of the preceding claims.

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